

# GRIGNARD METATHESIS (GRIM) METHOD FOR THE SYNTHESIS OF REGIOREGULAR POLY(3-ALKYLTHIOPHENES) WITH WELL-DEFINED MOLECULAR WEIGHTS

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## Introduction

Poly(3-alkylthiophenes) (PATs) represent an important class of conducting polymers that are soluble and processable, and widely used in the fabrication of organic semiconductor devices [1,2]. The initial synthesis of PATs proceeds through electrochemical or oxidative chemical polymerization methods [3,4]. These approaches yield polymers with various degrees of regioregularity due to the presence of configurational isomers (head-to-head, head-to-tail and tail-to-tail). In the past, it was shown that regiorandom polymers cannot adopt planar conformations, and irregular placement of the solubilizing alkyl side chains prevents efficient solid state packing and limits the material's physical properties [5-8].

Regioselective synthesis of PATs that contain almost exclusively head-to-tail couplings resulted in improved electrical conductivities and a greater effective conjugation length. The synthesis of regioregular PATs, first discovered by McCullough *et al.* [5,6] and was followed by others [9], resulted in the formation of defect-free, structurally homogeneous, head-to-tail coupled poly(3-alkylthiophenes) (HT-PATs) with greatly improved electronic and photonic properties over regiorandom analogues [10-12].

The Grignard Metathesis Method (GRIM) has been reported to successfully synthesize regioregular PATs as well [13,14]. The advantages of the GRIM method over the previously reported ones include the ease of preparation and purification of the thiophene monomers. Furthermore, the reaction does not require the use of cryogenic temperatures and can be carried out on large scale.

We have recently reported that the nickel-initiated cross-coupling polymerization (*e.g.*, McCullough method) proceeds *via* a chain growth mechanism and the molecular weight of PATs can be predicted by the molar ratio of monomer to Ni(dppp)Cl<sub>2</sub> [15]. Moreover, addition of various Grignard reagents (R'MgX) at the end of polymerization results in end-capping of regioregular PATs with R' end group, which leads to the synthesis of a variety of end-functionalized PATs [16].

We are reporting here a kinetic study of nickel initiated cross-coupling polymerization of PATs utilizing the GRIM method, which confirms that this reaction proceeds *via* a chain growth mechanism. PATs with well defined molecular weight and narrow molecular weight distribution can be readily synthesized.

## Experimental

**Polymerization Experiment.** GRIM polymerizations were performed as described previously [13, 14]. Ni(dppp)Cl<sub>2</sub> was used as initiator.

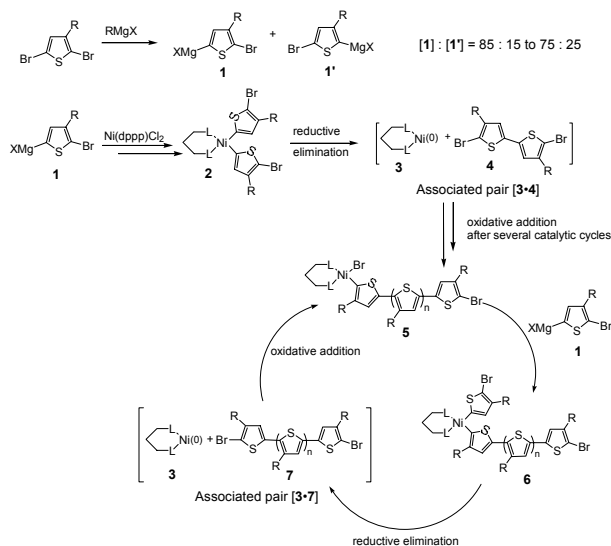
**Analyses.** GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethyl siloxane. Helium was the carrier gas (1 mL/min). GPC measurements were performed on a Waters 2690 separations module apparatus and a Waters 2487 dual  $\lambda$  absorbance detector with chloroform as the eluent (flow rate 1 mL/min, 35 °C,  $\lambda$ =254 nm) with a series of three Styragel columns (10<sup>4</sup>, 500, 100 Å; Polymer Standard Services). Toluene was used as internal standard and calibration based on polystyrene standards was applied for determination of molecular weights. <sup>1</sup>H NMR spectra of the polymer solutions in CDCl<sub>3</sub> were recorded on a Bruker Avance 500 MHz spectrometer.

## Results and discussion

The mechanism of the nickel initiated cross-coupling chain-growth polymerization is outlined in Scheme 1 [15]. Treatment of 2,5-dibromo-3-hexylthiophene with 1 equiv of Grignard reagent (RMgX) results in magnesium-halogen exchange reaction, also referred as Grignard Metathesis (GRIM). This reaction proceeds with a moderate degree of regioselectivity leading to a distribution of regiochemical isomers (**1**) and (**1'**) around 85:15.

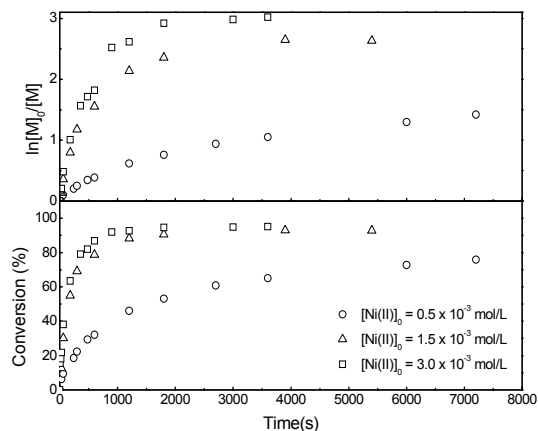
The GC-MS analysis after the addition of Ni(dppp)Cl<sub>2</sub> indicated that only isomer (**1**) is incorporated into the polymer, while isomer (**1'**) was not consumed.

The first step in the mechanism is the reaction of 2-bromo-5-halomagnesium-3-hexylthiophene monomer (**1**) with Ni(dppp)Cl<sub>2</sub> yielding the organonickel compound (**2**). We have proposed that the reductive elimination of (**2**) *immediately* results in the formation of an associated pair [**3**•**4**] of the tail-to-tail aryl halide dimer (**4**) and Ni(0) (**3**). The dimer (**4**) undergoes fast oxidative addition to the nickel center generating (**5**). Growth of the polymer chain occurs by insertion of one monomer at a time as shown in the reaction cycle (**5**→**6**→[**3**•**7**]→**5**), where Ni(dppp) moiety is incorporated into polymer chain as an end group [15].

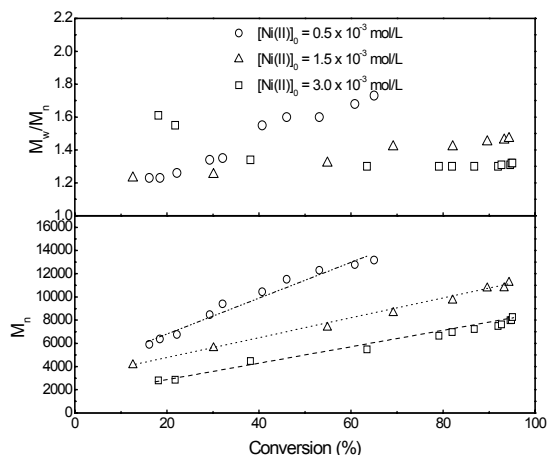


**Scheme 1.** Mechanism for the nickel initiated cross-coupling polymerization (GRIM method).

Several experiments were performed at variable Ni(dppp)Cl<sub>2</sub> concentration and constant monomer (**1**) concentration.

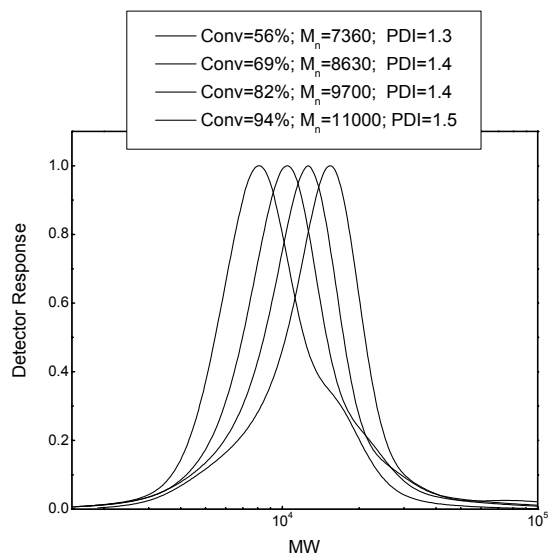


**Figure 1.** Conversion and logarithm of monomer concentration vs. time plots for 2-bromo-5-chloromagnesium-3-hexylthiophene polymerization at variable Ni(dppp)Cl<sub>2</sub> concentrations; [M]<sub>0</sub>=0.07 mol/L; 23-25 °C.



**Figure 2.** Dependence of molecular weights and polydispersities on conversion for 2-bromo-5-chloromagnesium-3-hexylthiophene polymerization at variable  $\text{Ni(dppp)Cl}_2$  concentrations  $[\text{M}]_0=0.07 \text{ mol/L}$ ; 23–25 °C.

The reaction rates increased with the increase in the  $\text{Ni(dppp)Cl}_2$  concentration (Figure 1). Molecular weight vs conversion plot (Figure 2) and the GPC traces (Figure 3) show the increase of molecular weight with conversion, which supports a chain growth mechanism for nickel-initiated cross-coupling polymerization (GRIM method). The molecular weight of the polymer is a function of the molar ratio of monomer (**1**) to  $\text{Ni(dppp)Cl}_2$  initiator (Figure 2). PATs with relatively narrow polydispersities ( $\text{PDI} < 1.5$ ) were obtained for the experiments performed at high concentrations of  $\text{Ni(dppp)Cl}_2$  (Figure 2).

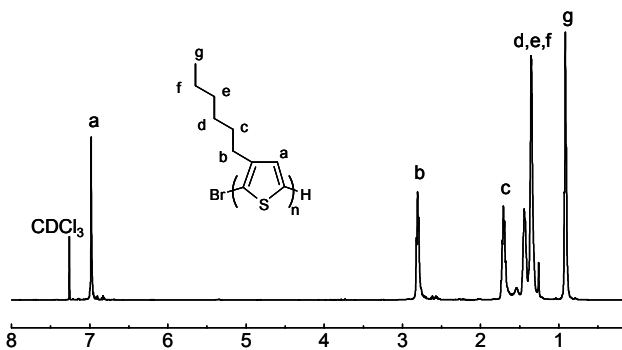


**Figure 3.** GPC traces for 2-bromo-5-chloromagnesium-3-hexylthiophene polymerization;  $[\text{Ni(II)}]_0=1.5 \times 10^{-3} \text{ mol/L}$ ;  $[\text{M}]_0=0.07 \text{ mol/L}$ ; 23–25 °C.

$^1\text{H}$  NMR spectroscopy was used for the estimation of the degree of regioregularity ( $\text{HT} > 98\%$ ) of synthesized poly(3-hexylthiophene) polymers (Figure 4).

## Conclusion

Synthesis of PATs with well-defined molecular weights and narrow PDIs opens a way towards tuning electrical and optical properties of conducting polymers.



**Figure 4.**  $^1\text{H}$  NMR spectrum of regioregular poly(3-hexylthiophene)

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